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INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P28786PC00		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/ZA 03/00187	International filing date (day/month/year) 19.12.2003	Priority date (day/month/year) 20.12.2002	
International Patent Classification (IPC) or both national classification and IPC B01J31/18, B01J31/24, C07C2/36, C07C11/02, C07C2/32			
Applicant SASOL TECHNOLOGY (PTY) LTD et al.			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 28 sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the opinion</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>			
Date of submission of the demand  19.05.2004		Date of completion of this report  08.04.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer  Thomas, D Telephone No. +49 89 2399-7837 	

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/ZA 03/00187

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

### Description, Pages

1-4, 6-10, 12-17, 35	as originally filed
5, 11, 18-34	received on 12.11.2004 with letter of 04.10.2004

### Claims, Numbers

1-47	filed with telefax on 16.02.2005
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/ZA 03/00187

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	15-17, 35-37
	No: Claims	1-14, 18-34, 38-47
Inventive step (IS)	Yes: Claims	15-17, 35-37
	No: Claims	1-14, 18-34, 38-47
Industrial applicability (IA)	Yes: Claims	1-47
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/ZA 03/00187

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

A reasonable statement concerning novelty and inventive step is at the present stage not possible (Problems with Article 6 PCT, s next paragraph)

Claims 15-17 as well as claim 35 - 37 are regarded to be novel and inventive.

**Certain defects in the international application**

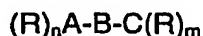
Present claim 1 describes a tetramerization process for olefines. The heteroatomic ligand used in said process is described by a markush formula with  $R^1$ - $R^4$  being a hydrocarbyl or heterohydrocarbyl groups.

The substitution pattern of  $R^1$ - $R^4$  is further restricted, but a clear definition of what is regarded to be the hydrocarbyl or heterohydrocarbyl group and what is regarded to be a substituent is missing.

(Where does the heterohydrocarbyl group end and where does the substituent start ? example:  $R^1 = (MeO)Ph$  or  $R^1 = Ph$  and Substituent = OMe ? )

1. A process for tetramerisation of olefins wherein an olefinic feedstream is contacted with a catalyst system which includes the combination of

- a transition metal compound; and
- a heteroatomic ligand described by the following general formula



wherein

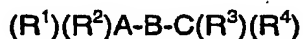
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different, and each R is independently selected from the group consisting of a hydrocarbyl group, a hetero hydrocarbyl group, a substituted hydrocarbyl group, and a substituted hetero hydrocarbyl group;

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a hydrocarbyl group, a hetero hydrocarbyl group, a substituted hydrocarbyl group, and a substituted hetero hydrocarbyl group;

any substituents that may be on one or more of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are non electron donating; and where  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently aromatic, including hetero aromatic, groups, not all the groups  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  have a substituent on the atom adjacent to the atom bound to A or C.

2. The process as claimed in claim 1, wherein the olefinic feedstream includes an  $\alpha$ -olefin and the product stream includes at least 30% of a tetramerised  $\alpha$ -olefin monomer.
3. The process as claimed in either one of claims 1 or 2, wherein the olefinic feedstream includes ethylene and the product stream includes at least 30% 1-octene.
4. The process as claimed in any one of claims 1 to 3, wherein the olefinic feedstream includes ethylene and wherein  $(C_6 + C_8) : (C_4 + C_{10})$  ratio in the product stream is more than 2.5:1.
5. The process as claimed in either one of claims 3 or 4, wherein ethylene is contacted with the catalyst system at a pressure of more than 1000 kPa (10 barg).
6. The process as claimed in any one of claims 1 to 5, wherein the heteroatomic ligand is described by the following general formula  $(R^1)(R^2)A-B-C(R^3)(R^4)$  wherein A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen; B is a linking group between A and C; and each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a hydrocarbyl group, a hetero hydrocarbyl group, a substituted hydrocarbyl group, and a substituted hetero hydrocarbyl group.
7. The process as claimed in claim 6, wherein the heteroatomic ligand is described by the following general formula  $(R^1)(R^2)A-B-C(R^3)(R^4)$  wherein A and C are independently selected from the group comprising of phosphorous, arsenic, antimony, bismuth and nitrogen; B is a linking group between A and C; and each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a non-aromatic hydrocarbyl group, a non-aromatic heterohydrocarbyl group, an aromatic hydrocarbyl group, an aromatic hetero hydrocarbyl group and a hetero aromatic hetero hydrocarbyl group.

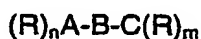
8. The process as claimed in either one of claims 6 or 7, wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently an aromatic group, including a hetero aromatic group and not all the groups  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  have a substituent on the atom adjacent to the atom bound to A or C.
9. The process as claimed in any one of claims 1 to 8, wherein each non electron donating substituent is non polar.
10. The process as claimed in any one of claims 1 to 9, wherein B is selected from the group consisting of: an organic linking group comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; an inorganic linking group comprising a single atom linking spacer and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine,  $-B(R^5)-$ ,  $-Si(R^5)_2-$ ,  $-P(R^5)-$  and  $-N(R^5)-$  where  $R^5$  is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom or a halogen.
11. The process as claimed in claim 10, wherein B is a single atom linking spacer.
12. The process as claimed in claim 10, wherein B is  $-N(R^5)-$ , wherein  $R^5$  is selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, a silyl group or a derivative thereof, and an aryl group substituted with any of these substituents.
13. The process as claimed in any one of claims 1 to 12, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
14. The process as claimed in any one of claims 1 to 12, wherein each of A and C is phosphorus.
15. The process as claimed in claim 12, wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of benzyl, phenyl, tolyl,

xylyl, mesityl, biphenyl, naphthyl, anthracenyl, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuran group.

16. The process as claimed in claim 15, wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a phenyl, tolyl, biphenyl, naphthyl, thiophenyl and ethyl group.
17. The process as claimed in claim 1 wherein the ligand is selected from the group consisting of  
 $(\text{phenyl})_2\text{PN}(\text{methyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}(\text{pentyl})\text{P}(\text{phenyl})_2$ ,  
 $(\text{phenyl})_2\text{PN}(\text{phenyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}(\text{p-methoxyphenyl})\text{P}(\text{phenyl})_2$ ,  
 $(\text{phenyl})_2\text{PN}(\text{p-butylphenyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}((\text{CH}_2)_3\text{-N-morpholine})\text{P}(\text{phenyl})_2$ ,  
 $(\text{phenyl})_2\text{PN}(\text{Si}(\text{CH}_3)_3)\text{P}(\text{phenyl})_2$ ,  
 $((\text{phenyl})_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}$ ,  $(\text{ethyl})_2\text{PN}(\text{methyl})\text{P}(\text{ethyl})_2$ ,  
 $(\text{ethyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ ,  $(\text{ethyl})(\text{phenyl})\text{PN}(\text{methyl})\text{P}(\text{ethyl})(\text{phenyl})$ ,  
 $(\text{ethyl})(\text{phenyl})\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ ,  
 $(\text{phenyl})_2\text{P}(=\text{Se})\text{N}(\text{isopropyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PCH}_2\text{CH}_2\text{P}(\text{phenyl})_2$ ,  $(\text{o-ethylphenyl})(\text{phenyl})\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ ,  $(\text{o-methylphenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{o-methylphenyl})(\text{phenyl})$ ,  
 $(\text{phenyl})_2\text{PN}(\text{benzyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}(1\text{-cyclohexyl-ethyl})\text{P}(\text{phenyl})_2$ ,  
 $(\text{phenyl})_2\text{PN}[\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe}_3)]\text{P}(\text{phenyl})_2$ ,  
 $(\text{phenyl})_2\text{PN}(\text{cyclohexyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}(2\text{-methylcyclohexyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}(\text{allyl})\text{P}(\text{phenyl})_2$ ,  $(2\text{-naphthyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-naphthyl})_2$ ,  $(\text{p-biphenyl})_2\text{PN}(\text{methyl})\text{P}(\text{p-biphenyl})_2$ ,  
 $(\text{p-methylphenyl})_2\text{PN}(\text{methyl})\text{P}(\text{p-methylphenyl})_2$ ,  $(2\text{-thiophenyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-thiophenyl})_2$ ,  
 $(\text{phenyl})_2\text{PN}(\text{methyl})\text{N}(\text{methyl})\text{P}(\text{phenyl})_2$ ,  $(\text{m-methylphenyl})_2\text{PN}(\text{methyl})\text{P}(\text{m-methylphenyl})_2$ ,  
 $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ , and  
 $(\text{phenyl})_2\text{P}(=\text{S})\text{N}(\text{isopropyl})\text{P}(\text{phenyl})_2$ .
18. The process of any one of claims 1 to 17 wherein the catalyst system is prepared by combining in any order the heteroatomic ligand, the transition metal compound and an activator.

19. The process of any one of claims 1 to 17 wherein the catalyst system is a pre-formed coordination complex prepared by combining the heteroatomic ligand and the transition metal compound and wherein the pre-formed coordination complex is added to the olefinic feedstream and an activator.
20. The process as claimed in any one of claims 1 to 19, wherein the transition metal in the transition metal compound is selected from the group consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
21. The process as claimed in claim 20, wherein the transition metal is chromium.
22. The process as claimed in any one of claims 1 to 21, wherein the transition metal compound is selected from the group consisting of an inorganic salt, an organic salt, a co-ordination complex and organometallic complex.
23. The process as claimed in claim 22, wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.
24. The process as claimed in claim 23, wherein the transition metal is a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.
25. The process as claimed in any one of claims 1 to 24, wherein the transition metal from the transition metal compound and the heteroatomic ligand are combined to provide a transition metal/ligand ratio from about 0.01:100 to 10 000:1.
26. The process as claimed in any one of claims 1 to 25, wherein the catalyst systems includes an activator selected from the group consisting of an organoaluminium compound, an organoboron compound, an organic salt, such as methyl lithium and methylmagnesium bromide, an inorganic acid and salt, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.

27. The process as claimed in claims 26, wherein the activator is an alkylaluminoxane.
28. The process as claimed in claim 27, wherein the transition metal and the aluminoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 10 000:1.
29. A catalyst system which includes the combination of
- a transition metal compound; and
  - a heteroatomic ligand described by the following general formula



wherein

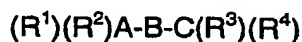
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different, and each R is independently selected from the group consisting of a hydrocarbyl group, a hetero hydrocarbyl group, a substituted hydrocarbyl group, and a substituted hetero hydrocarbyl group;

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a hydrocarbyl group, a hetero hydrocarbyl group, a substituted hydrocarbyl group, and a substituted hetero hydrocarbyl group;

any substituents that may be on one or more of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are non electron donating; and where  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently aromatic, including hetero aromatic, groups, not all the groups  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  have a substituent on the atom adjacent to the atom bound to A or C.

30. The catalyst system of claim 29 which is a tetramerisation catalyst system.
31. The catalyst system of either one of claims 29 or 30 wherein the heteroatomic ligand is described by the following general formula  $(R^1)(R^2)A-B-C(R^3)(R^4)$  wherein A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen; B is a linking group between A and C; and each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a hydrocarbyl group, a hetero hydrocarbyl group, a substituted hydrocarbyl group, and a substituted hetero hydrocarbyl group.
32. The catalyst system of any one of claims 29 to 31 wherein B is selected from the group consisting of an organic linking group comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; an inorganic linking group comprising a single atom linking spacer; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine,  $-B(R^5)-$ ,  $-Si(R^5)_2-$ ,  $-P(R^5)-$  and  $-N(R^5)-$  where  $R^5$  is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom or a halogen.
33. The catalyst system of claim 32 wherein B is  $-N(R^5)-$ , wherein  $R^5$  is selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, a silyl group or a derivative thereof, and an aryl group substituted with any of these substituents.

34. The catalyst system of any one of claims 29 to 33 wherein each of A and C is independently phosphorus .
35. The catalyst system of any one of claims 29 to 34 wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is independently selected from the group consisting of benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranyl group.
36. The catalyst system of claim 35 wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently selected from the group consisting of a phenyl, tolyl, biphenyl, naphthyl, thiophenyl and ethyl group.
37. The catalyst system of claim 29 wherein the ligand is selected from the group consisting of  
 (phenyl)<sub>2</sub>PN(methyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(pentyl)P(phenyl)<sub>2</sub>,  
 (phenyl)<sub>2</sub>PN(phenyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(*p*-methoxyphenyl)P(phenyl)<sub>2</sub>,  
 (phenyl)<sub>2</sub>PN(*p*-<sup>t</sup>butylphenyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN((CH<sub>2</sub>)<sub>3</sub>-N-morpholine)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(Si(CH<sub>3</sub>)<sub>3</sub>)P(phenyl)<sub>2</sub>,  
 (((phenyl)<sub>2</sub>P)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)N, (ethyl)<sub>2</sub>PN(methyl)P(ethyl)<sub>2</sub>,  
 (ethyl)<sub>2</sub>PN(isopropyl)P(phenyl)<sub>2</sub>, (ethyl)(phenyl)PN(methyl)P(ethyl)(phenyl),  
 (ethyl)(phenyl)PN(isopropyl)P(phenyl)<sub>2</sub>,  
 (phenyl)<sub>2</sub>P(=Se)N(isopropyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(phenyl)<sub>2</sub>, (*o*-ethylphenyl)(phenyl)PN(isopropyl)P(phenyl)<sub>2</sub>, (*o*-methylphenyl)<sub>2</sub>PN(isopropyl)P(*o*-methylphenyl)(phenyl),  
 (phenyl)<sub>2</sub>PN(benzyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(1-cyclohexyl-ethyl)P(phenyl)<sub>2</sub>,  
 (phenyl)<sub>2</sub>PN[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>]P(phenyl)<sub>2</sub>,  
 (phenyl)<sub>2</sub>PN(cyclohexyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(2-methylcyclohexyl)P(phenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(allyl)P(phenyl)<sub>2</sub>, (2-naphthyl)<sub>2</sub>PN(methyl)P(2-naphthyl)<sub>2</sub>, (*p*-biphenyl)<sub>2</sub>PN(methyl)P(*p*-biphenyl)<sub>2</sub>, (*p*-methylphenyl)<sub>2</sub>PN(methyl)P(*p*-methylphenyl)<sub>2</sub>, (2-thiophenyl)<sub>2</sub>PN(methyl)P(2-thiophenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(methyl)N(methyl)P(phenyl)<sub>2</sub>, (*m*-methylphenyl)<sub>2</sub>PN(methyl)P(*m*-methylphenyl)<sub>2</sub>, (phenyl)<sub>2</sub>PN(isopropyl)P(phenyl)<sub>2</sub>, and (phenyl)<sub>2</sub>P(=S)N(isopropyl)P(phenyl)<sub>2</sub>.

38. The catalyst system of any one of claims 29 to 37 wherein the transition metal in the transition metal compound is selected from any one of the group consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
39. The catalyst system of claim 38, wherein the transition metal is chromium.
40. The catalyst system of any one of claims 29 to 40 wherein the transition metal compound is selected from the group consisting of an inorganic salt, organic salt, a co-ordination complex and organometallic complex.
41. The catalyst system of claim 40 wherein wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.
42. The catalyst system of any one of claims 29 to 41 wherein the transition metal from the transition metal compound and the heteroatomic ligand are combined to provide a transition metal/ligand ratio from about 0.01:100 to 10 000:1.
43. The catalyst system of any one of claims 29 to 42 which includes an activator.
44. The catalyst system of claim 43 wherein the activator is an alkylaluminoxane.
45. The catalyst system of claim 44 wherein the transition metal and the aluminoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 10 000:1.
46. Use of a catalyst system as claimed in any one of claims 29 to 45 for the tetramerisation of olefins.
47. Use of a catalyst system as claimed in any one of claims 29 to 46 for the tetramerisation of ethylene.



The reaction products as described herein, may be prepared using the disclosed catalyst system by a homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The process may also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, heptane, methylcyclohexane, methylcyclopentane, cyclohexane, 1-hexene, 1-octene, ionic liquids and the like.

The process may be carried out at pressures from atmospheric to 50 000 kPa (500 barg). Ethylene pressures in the range of 1000–7000 kPa (10-70 barg) are preferred. Particularly preferred pressures range from 3000–5000 kPa (30-50 barg).

The process may be carried out at temperatures from -100 °C to 250 °C. Temperatures in the range of 15-130 °C are preferred. Particularly preferred temperatures range from 35-100°C.

In a preferred embodiment of the invention, the heteroatomic coordination complex and reaction conditions are selected such that the yield of 1-octene from ethylene is greater than 30 mass %, preferably greater than 35 mass %. In this regard yield refers to grams of 1-octene formed per 100g of total reaction product formed.

In addition to 1-octene, the process may also yield different quantities of 1-butene, 1-hexene, methylcyclopentane, methylene cyclopentane, propylcyclopentane, propylene cyclopentane, specific higher oligomers and polyethylene, depending on the nature of the heteroatomic ligand and the reaction conditions. A number of these products cannot be formed *via* conventional ethylene oligomerisation and trimerisation technologies in the yields observed in the present invention.

**Example 1c): Preparation of Bis(phenyl) phosphorus chloride**

The Grignard reagent was added to N,N-diisopropylphosphoramid dichloride (6.64 ml, 36 mmol) in THF (100 ml) at 0 °C. After stirring at room temperature overnight the mixture was diluted with cyclohexane (200 ml) and dry HCl gas was bubbled through the solution for 0.5 hours. After filtration of the precipitate, the solvent was removed to give a mixture of the phosphine chloride and bromide in an 80% yield. This crude product was not isolated and all was used in the next step.

**Example 1d): Preparation of the (phenyl)<sub>2</sub>PN(isopropyl)P(phenyl)<sub>2</sub> ligand**

To a solution of the crude Bis(phenyl) phosphorus chloride (28.8 mmol calculated from crude reaction mixture) in DCM (80 ml) and triethylamine (15 ml) at 0 °C was added isopropylamine (1.11 ml, 13 mmol). The reaction was stirred for 30 min after which the ice bath was removed. After stirring for a total of 14 hrs the solution was filtered to remove the triethylammonium salt formed. The product was isolated after crystallisation in a 90 % yield. <sup>31</sup>P {H} NMR: 49.0 ppm (broad singlet).

**Example 2: Ethylene tetramerisation reaction using CrCl<sub>3</sub>(tetrahydrofuran)<sub>3</sub>, (phenyl)<sub>2</sub>PN(methyl)P(phenyl)<sub>2</sub> and MAO**

A solution of 29.0 mg of (phenyl)<sub>2</sub>PN(methyl)P(phenyl)<sub>2</sub> (0.073 mmol) in 5 ml of toluene was added to a solution of 12.4 mg CrCl<sub>3</sub>(tetrahydrofuran)<sub>3</sub> (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 80°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 85°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 60 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid products. These solid products were dried overnight in an oven at

100°C and then weighed. The mass of total product was 31.86 g. The product distribution of this example is summarised in Table 1.

**Example 3: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{methyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 22.4 mg of  $(\text{phenyl})_2\text{PN}(\text{methyl})\text{P}(\text{phenyl})_2$  (0.056 mmol) in 5 ml of toluene was added to a solution of 12.4 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 80°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 85°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 60 min, and the procedure of Example 2 above was employed. The product mass was 28.76 g. The product distribution of this example is summarised in Table 1.

**Example 4: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{methyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 26.3 mg of  $(\text{phenyl})_2\text{PN}(\text{methyl})\text{P}(\text{phenyl})_2$  (0.066 mmol) in 3 ml of toluene was added to a solution of 12.4 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.033 mmol) in 17 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 60 min, and the procedure of Example 2 above was employed. The product mass was 47.23 g. The product distribution of this example is summarised in Table 1.

**Example 5: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{pentyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 30.0 mg of  $(\text{phenyl})_2\text{PN}(\text{pentyl})\text{P}(\text{phenyl})_2$  (0.074 mmol) in 10 ml of toluene was added to a solution of 12.4 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 10.6 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor

temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 60 min, and the procedure of Example 2 above was employed. The product mass was 74.84 g. The product distribution of this example is summarised in Table 1.

**Example 6: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{benzyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 30.7 mg of  $(\text{phenyl})_2\text{PN}(\text{benzyl})\text{P}(\text{phenyl})_2$  (0.065 mmol) in 10 ml of toluene was added to a solution of 12.4 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 10.6 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 180 min, and the procedure of Example 2 above was employed. The product mass was 22.08 g. The product distribution of this example is summarised in Table 1.

**Example 7: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{phenyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 34.9 mg of  $(\text{phenyl})_2\text{PN}(\text{phenyl})\text{P}(\text{phenyl})_2$  (0.076 mmol) in 10 ml of toluene was added to a solution of 13.5 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.036 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 10.6 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 180 min, and the procedure of Example 2 above was employed. The product mass was 48.21 g. The product distribution of this example is summarised in Table 1.

**Example 8: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(p\text{-methoxy-phenyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 30.6 mg of  $(\text{phenyl})_2\text{PN}(p\text{-methoxyphenyl})\text{P}(\text{phenyl})_2$  (0.062 mmol) in 10 ml of toluene was added to a solution of 12.4 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor

(autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 10.6 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 60 min, and the procedure of Example 2 above was employed. The product mass was 7.01 g. The product distribution of this example is summarised in Table 1.

**Example 9: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(p\text{-butylphenyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 29.3mg of  $(\text{phenyl})_2\text{PN}(p\text{-butylphenyl})\text{P}(\text{phenyl})_2$  (0.062 mmol) in 10 ml of toluene was added to a solution of 12.4 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 10.6 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 180 min, and the procedure of Example 2 above was employed. The product mass was 62.15 g. The product distribution of this example is summarised in Table 1.

**Example 10: Ethylene tetramerisation reaction using  $\text{Cr}(\text{2-ethylhexanoate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{allyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 27.6 mg of  $(\text{phenyl})_2\text{PN}(\text{allyl})\text{P}(\text{phenyl})_2$  (0.066 mmol) in 10 ml of toluene was added to a solution of 22.8 mg  $\text{Cr}(\text{2-ethylhexanoate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 12.68 g. The product distribution of this example is summarised in Table 1.

**Example 11: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}[(\text{CH}_2)_3\text{Si}(\text{OMe})_3]\text{P}(\text{phenyl})_2$  and MAO**

A solution of 36.1 mg of  $(\text{phenyl})_2\text{PN}[(\text{CH}_2)_3\text{Si}(\text{OMe})_3]\text{P}(\text{phenyl})_2$  (0.066 mmol) in 15 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol)

in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (75ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 72.96 g. The product distribution of this example is summarised in Table 1.

**Example 12: Ethylene tetramerisation reaction using Cr(acetylacetonate)<sub>3</sub>, (phenyl)<sub>2</sub>PN[(CH<sub>2</sub>)<sub>3</sub>-N-morpholine]P(phenyl)<sub>2</sub> and MAO**

A solution of 33.8 mg of (phenyl)<sub>2</sub>PN[(CH<sub>2</sub>)<sub>3</sub>-N-morpholine]P(phenyl)<sub>2</sub> (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg Cr(acetylacetonate)<sub>3</sub> (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 22.2 g. The product distribution of this example is summarised in Table 1.

**Example 13: Ethylene tetramerisation reaction using CrCl<sub>3</sub>(tetrahydrofuran)<sub>3</sub>, (phenyl)<sub>2</sub>PN(*i*-propyl)P(phenyl)<sub>2</sub> and MAO**

A solution of 26.1 mg of (phenyl)<sub>2</sub>PN(*i*-propyl)P(phenyl)<sub>2</sub> (0.061 mmol) in 10 ml of toluene was added to a solution of 11.6 mg CrCl<sub>3</sub>(tetrahydrofuran)<sub>3</sub> (0.031 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 10.6 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 180 min, and the procedure of Example 2 above was employed. The product mass was 56.44 g. The product distribution of this example is summarised in Table 1.

**Example 14: Ethylene tetramerisation reaction using CrCl<sub>3</sub>(tetrahydrofuran)<sub>3</sub>, (phenyl)<sub>2</sub>PN(*i*-propyl)P(phenyl)<sub>2</sub> and MAO**

A solution of 17.1 mg of  $(\text{phenyl})_2\text{PN}(\text{'propyl})\text{P}(\text{phenyl})_2$  (0.04 mmol) in 10 ml of toluene was added to a solution of 7.5 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.02 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.0 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 43°C, while the ethylene pressure was kept at 4500 kPa (45 barg). The reaction was terminated after 60 min, and the procedure of Example 2 above was employed. The product mass was 39.98 g. The product distribution of this example is summarised in Table 1.

**Example 15: Ethylene tetramerisation reaction using  $\text{Cr}(\text{2-ethylhexanoate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{'propyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 18.8 mg of  $(\text{phenyl})_2\text{PN}(\text{'propyl})\text{P}(\text{phenyl})_2$  (0.022 mmol) in 10 ml of toluene was added to a solution of 7.6 mg  $\text{Cr}(\text{2-ethylhexanoate})_3$  (0.011 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml) and MAO (methylaluminoxane, 3.3 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 50 min, and the procedure of Example 2 above was employed. The product mass was 64.71 g. The product distribution of this example is summarised in Table 1.

**Example 16: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{'propyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 28.2 mg of  $(\text{phenyl})_2\text{PN}(\text{'propyl})\text{P}(\text{phenyl})_2$  (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 14 min, and the procedure of Example 2 above was employed. The product mass was 75.80 g. The product distribution of this example is summarised in Table 1.

**Example 17: Ethylene tetramerisation reaction using Cr(acetylacetonate)<sub>3</sub>, (phenyl)<sub>2</sub>PN(<sup>i</sup>propyl)P(phenyl)<sub>2</sub> and EAO/TMA**

A solution of 28.2 mg of (phenyl)<sub>2</sub>PN(<sup>i</sup>propyl)P(phenyl)<sub>2</sub> (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg Cr(acetylacetonate)<sub>3</sub> (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml), EAO (ethylaluminumoxane, 33 mmol) and TMA (trimethylaluminum, 8.3 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 37 min, and the procedure of Example 2 above was employed. The product mass was 29.03 g. The product distribution of this example is summarised in Table 1.

**Example 18: Ethylene tetramerisation reaction using Cr(acetylacetonate)<sub>3</sub>, (phenyl)<sub>2</sub>PN(<sup>i</sup>propyl)P(phenyl)<sub>2</sub> and MMAO**

A solution of 17.1 mg of (phenyl)<sub>2</sub>PN(<sup>i</sup>propyl)P(phenyl)<sub>2</sub> (0.04 mmol) in 10 ml of toluene was added to a solution of 7.0 mg Cr(acetylacetonate)<sub>3</sub> (0.02 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml) and MAO (modified methylaluminumoxane, Akzo Nobel MMAO-3A, 6.0 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 15 min, and the procedure of Example 2 above was employed. The product mass was 74.11 g. The product distribution of this example is summarised in Table 1.

**Example 19: Ethylene tetramerisation reaction using Cr(acetylacetonate)<sub>3</sub>, (phenyl)<sub>2</sub>PN(<sup>i</sup>propyl)P(phenyl)<sub>2</sub> and supported MAO**

A solution of 28.2 mg of (phenyl)<sub>2</sub>PN(<sup>i</sup>propyl)P(phenyl)<sub>2</sub> (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg Cr(acetylacetonate)<sub>3</sub> (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature. 3.9 g supported MAO (MAO on SiO<sub>2</sub>, Crompton, containing 11.3 mmol MAO) was suspended in 30 ml of toluene and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (50 ml) and TMA (trimethylaluminum, 3.3 mmol) at 40°C. The catalyst solution was then added to the pressure reactor. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The

reaction was terminated after 15 min, and the procedure of Example 2 above was employed. The product mass was 43.61 g. The product distribution of this example is summarised in Table 1.

**Example 20: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 18.8 mg of  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  (0.044 mmol) in 6.4 ml of cumene was added to a solution of 7.7 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.022 mmol) in 8 ml cumene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 1000 ml pressure reactor (autoclave) containing a mixture of cumene (180 ml) and MAO (methylaluminoxane, 4.4 mmol, 10 % solution in toluene) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 25 min, and the procedure of Example 2 above was employed. The product mass was 118.78 g. The product distribution of this example is summarised in Table 1.

**Example 21: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 11.1 mg of  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  (0.026 mmol) in 10 ml of ethylbenzene was added to a solution of 7.0 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.02 mmol) in 10 ml ethylbenzene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of ethylbenzene (76 ml) and MAO (methylaluminoxane, 4.0 mmol, 7% solution in toluene) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 10 min, and the procedure of Example 2 above was employed. The product mass was 70.6 g. The product distribution of this example is summarised in Table 1.

**Example 22: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 5.8 mg of  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  (0.014 mmol) in 10 ml of cyclohexane was added to a solution of 3.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.01 mmol) in 10 ml cyclohexane in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature. This solution and a solution of MAO (methylaluminoxane, 2.0 mmol, 7% solution in toluene) was added via a burette to a 1000 ml pressure reactor

(autoclave) containing cyclohexane (170 ml) at 45°C and being pressurised at 40 bar. After the addition, the ethylene pressure was maintained at 4500 kPa (45 barg) and the temperature controlled at 45°C. The reaction was terminated after 39 min, and the procedure of Example 2 above was employed. The product mass was 307.30 g. The product distribution of this example is summarized in Table 1.

**Example 23: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 11.6 mg of  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  (0.026 mmol) in 10 ml of cumene was added to a solution of 7.4 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.02 mmol) in 10 ml cumene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature. This solution and a solution of MAO (methylaluminoxane, 2.8 mmol, 7% solution in toluene) was added via a burette to a 1000 ml pressure reactor (autoclave) containing cumene (180 ml) at 45°C and being pressurised at 40 bar. After the addition, the ethylene pressure was maintained at 4500 kPa (45 barg) and the temperature controlled at 45°C. The reaction was terminated after 75 min, and the procedure of Example 2 above was employed. The product mass was 308.83 g. The product distribution of this example is summarised in Table 1.

**Example 24: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(2\text{-naphthyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-naphthyl})_2$  and MAO**

A solution of 39.6 mg of  $(2\text{-naphthyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-naphthyl})_2$  (0.066 mmol) in 15 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (75ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 3000 kPa (30 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 45.18 g. The product distribution of this example is summarised in Table 1.

**Example 25: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(p\text{-biphenyl})_2\text{PN}(\text{methyl})\text{P}(p\text{-biphenyl})_2$  and MAO**

A solution of 47.0 mg of  $(p\text{-biphenyl})_2\text{PN}(\text{methyl})\text{P}(p\text{-biphenyl})_2$  (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient

temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 26.41 g. The product distribution of this example is summarised in Table 1.

**Example 26: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ , (m-methylphenyl) $_2\text{PN}(\text{methyl})\text{P}(\text{m-methylphenyl})_2$  and MAO**

A solution of 30.1 mg of (m-methylphenyl) $_2\text{PN}(\text{methyl})\text{P}(\text{m-methylphenyl})_2$  (0.066 mmol) in 15 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (75ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 6500 kPa (65 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 52.34 g. The product distribution of this example is summarised in Table 1.

**Example 27: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ , (p-methylphenyl) $_2\text{PN}(\text{methyl})\text{P}(\text{p-methylphenyl})_2$  and MAO**

A solution of 30.1 mg of (p-methylphenyl) $_2\text{PN}(\text{methyl})\text{P}(\text{p-methylphenyl})_2$  (0.066 mmol) in 15 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (75ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 4500 kPa (45 barg). The reaction was terminated after 15 min, and the procedure of Example 2 above was employed. The product mass was 80.59 g. The product distribution of this example is summarised in Table 1.

**Example 28: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ , (o-ethylphenyl)(Ph)PN('propyl)PPh $_2$  and MAO**

A solution of 30.1 mg of (o-ethylphenyl)(Ph)PN(*i*-propyl)PPh<sub>2</sub> (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg Cr(acetylacetonate)<sub>3</sub> (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 14 min, and the procedure of Example 2 above was employed. The product mass was 63.78 g. The product distribution of this example is summarised in Table 1.

**Example 29: Ethylene tetramerisation reaction using Cr(acetylacetonate)<sub>3</sub>, (phenyl)<sub>2</sub>P(=S)N(*i*-propyl)P(phenyl)<sub>2</sub> and MAO**

A solution of 30.3 mg of (phenyl)<sub>2</sub>P(=S)N(*i*-propyl)P(phenyl)<sub>2</sub> (0.066 mmol) in 15 ml of toluene was added to a solution of 11.5 mg Cr(acetylacetonate)<sub>3</sub> (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (75ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 33.06 g. The product distribution of this example is summarised in Table 1.

**Example 30: Ethylene tetramerisation reaction using Cr(acetylacetonate)<sub>3</sub>, (phenyl)<sub>2</sub>PN(*i*-propyl)P(phenyl)<sub>2</sub> and MAO**

A solution of 11.6 mg of (phenyl)<sub>2</sub>PN(*i*-propyl)P(phenyl)<sub>2</sub> (0.026 mmol) in 10 ml of cumene was added to a solution of 7.4 mg Cr(acetylacetonate)<sub>3</sub> (0.02 mmol) in 10 ml cumene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature. This solution and a solution of MAO (methylaluminoxane, 4.0 mmol, 7% solution in toluene) was added via a burette to a 1000 ml pressure reactor (autoclave) containing a mixture of cumene (80 ml) and 1-octene (80 ml) at 45°C and being pressurised at 40 bar. After the addition, the ethylene pressure was maintained at 4500 kPa (45 barg) and the temperature controlled at 45°C. The reaction was terminated after 45 min, and the procedure of Example 2 above was employed. The product mass was 405.87 g. The product distribution of this example is summarised in Table 1.

**Example 31: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{methyl})\text{N}(\text{methyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 28.3 mg of  $(\text{phenyl})_2\text{PN}(\text{methyl})\text{N}(\text{methyl})\text{P}(\text{phenyl})_2$  (0.066 mmol) in 15 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (75ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The liquid product mass was 22.45 g. The product distribution of this example is summarised in Table 1.

**Example 32: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(2\text{-thiophenyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-thiophenyl})_2$  and MAO**

A solution of 37.2 mg of  $(2\text{-thiophenyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-thiophenyl})_2$  (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 14.7 g. The product distribution of this example is summarised in Table 1.

**Example 33: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 5.8 mg of  $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$  (0.015 mmol) in 10 ml of cyclohexane was added to a solution of 3.8 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.011 mmol) in 10 ml cyclohexane in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature. 1.8 mmol of MAO (methylaluminoxane, 7% solution in toluene) was added and the mixture was stirred for 5 min. This solution was added via a burette to a 1000 ml pressure reactor (autoclave) containing cyclohexane (180 ml) at 45°C and being pressurised at 4000 kPa (40 bar). After the addition, the ethylene pressure was maintained at 4500 kPa (45 barg) and the temperature controlled at 45°C. The reaction was terminated after 60 min, and the procedure of Example 2 above was employed. The

product mass was 297.69 g. The product distribution of this example is summarised in Table 1.

**Example 34: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{SiMe}_3)\text{P}(\text{phenyl})_2$  and MAO**

A solution of 39.8 mg of  $(\text{phenyl})_2\text{PN}(\text{SiMe}_3)\text{P}(\text{phenyl})_2$  (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 26.9 g. The product distribution of this example is summarised in Table 1.

**Example 35: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $[(\text{phenyl}_2\text{P})_2\text{NCH}_2\text{CH}_2]\text{N}$  and MAO**

A solution of 62.5 mg of  $[(\text{phenyl}_2\text{P})_2\text{NCH}_2\text{CH}_2]\text{N}$  (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 65°C, while the ethylene pressure was maintained at 3000 kPa (30 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 2.5 g. The product distribution of this example is summarised in Table 1.

**Example 36: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(o\text{-methylphenyl})_2\text{PN}(\text{'propyl})\text{P}(o\text{-methylphenyl})(\text{phenyl})$  and MAO**

A solution of 11.7 mg of  $(o\text{-methylphenyl})_2\text{PN}(\text{'propyl})\text{P}(o\text{-methylphenyl})(\text{phenyl})$  (0.026 mmol) in 10 ml of toluene was added to a solution of 7.7 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.022 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 6.6 mmol) at 40°C. The pressure reactor was charged with

ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 55.45 g. The product distribution of this example is summarised in Table 1.

**Example 37. Preparation of  $[\text{Cr}\{(\text{phenyl})_2\text{PN}(\text{phenyl})\text{P}(\text{phenyl})_2\}\text{Cl}_2(\mu\text{-Cl})]_2$**

$(\text{phenyl})_2\text{PN}(\text{phenyl})\text{P}(\text{phenyl})_2$  (0.273g, 0.591 mmol) and  $\text{CrCl}_3(\text{thf})_3$  (0.206g, 0.550 mmol) were taken up in toluene (25 ml) and heated to 80°C overnight, resulting in the precipitation of a blue powder. After cooling to room temperature, the toluene was filtered from the precipitate and the product washed twice with petroleum ether (10 ml). Drying under vacuum yielded 0.303g (89%). Calculated for  $\text{C}_{60}\text{H}_{50}\text{N}_2\text{P}_4\text{Cr}_2\text{Cl}_6$  (found): C, 58.13 (57.98); H, 4.07 (3.97); N, 2.26 (2.12) %. Magnetic moment 4.06 BM per Cr (5.74 BM per dimer). Figure 1 shows the structure of the complex as obtained by single crystal X-ray analysis.

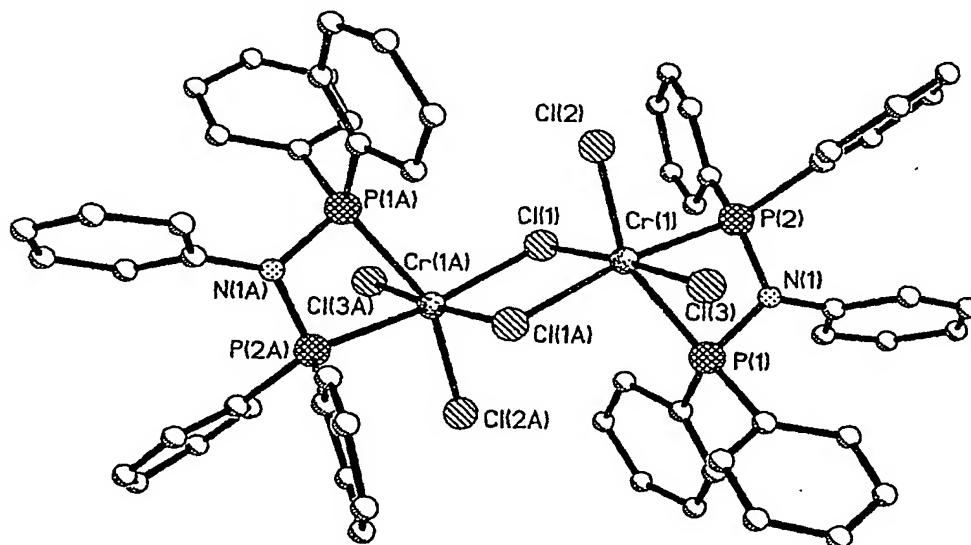


Figure 1.

**Example 38: Ethylene tetramerisation reaction using  $[\text{Cr}\{(\text{phenyl})_2\text{PN}(\text{phenyl})\text{P}(\text{phenyl})_2\}\text{Cl}_2(\mu\text{-Cl})]_2$  and MAO**

A suspension of  $[\text{Cr}\{(\text{phenyl})_2\text{PN}(\text{phenyl})\text{P}(\text{phenyl})_2\}\text{Cl}_2(\mu\text{-Cl})]_2$  (0.0125g, 0.020 mmol of Cr) in 20 ml of toluene was transferred to a 300 ml pressure reactor (autoclave)

containing toluene (100 ml) and MAO (6.0 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4000 kPa (40 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 4.61 g. The product distribution of this example is summarised in Table 1.

**Example 39. Preparation of the (ethyl)<sub>2</sub>PN(methyl)P(ethyl)<sub>2</sub> ligand**

Methylamine (3.1 ml of 2M solution, 6.2 mmol) in toluene (25 ml) was added slowly to a solution of chlorodiethylphosphine (1.582g, 12.7 mmol) in toluene (15 ml) and triethylamine (5 ml). The mixture was stirred overnight before being filtered through a glass fibre filter. The solvents were removed under vacuum and 10 ml of water was added. The product was extracted in petroleum ether (3 x 5 ml) and organics combined. Removal of the solvent under vacuum yielded 1.046g (81%) of the product. <sup>31</sup>P {H} NMR: 68 ppm.

**Example 40: Ethylene tetramerisation reaction using Cr(2-ethylhexanoate)<sub>3</sub>, (ethyl)<sub>2</sub>PN(methyl)P(ethyl)<sub>2</sub> and MAO**

A solution of Cr(2-ethylhexanoate)<sub>3</sub> (0.002M in toluene, 10 ml, 0.020 mmol) and a solution of (ethyl)<sub>2</sub>PN(methyl)P(ethyl)<sub>2</sub> (0.005M in toluene, 4.1 ml, 0.0205 mmol) were added to a 300 ml pressure reactor (autoclave) containing toluene (100 ml) and MAO (6.0 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4000 kPa (40 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 2.26 g. The product distribution of this example is summarised in Table 1.

**Example 41. Preparation of [Cr{(ethyl)<sub>2</sub>PN(methyl)P(ethyl)<sub>2</sub>}Cl<sub>2</sub>(μ-Cl)]<sub>2</sub>**

The procedure of example 38 was followed using (ethyl)<sub>2</sub>PN(methyl)P(ethyl)<sub>2</sub> (0.362g, 1.75 mmol) and CrCl<sub>3</sub>(thf)<sub>3</sub> (0.594g, 1.58 mmol). A yield of 0.520g (90%) was obtained. Calculated for C<sub>18</sub>H<sub>46</sub>N<sub>2</sub>P<sub>4</sub>Cr<sub>2</sub>Cl<sub>6</sub> (found): C, 29.57 (29.62); H, 6.34 (6.45); N, 3.83 (3.87) %. Magnetic moment 3.86 BM per Cr (5.46 BM per dimer).

**Example 42: Ethylene tetramerisation reaction using [Cr{(ethyl)<sub>2</sub>PN(methyl)P(ethyl)<sub>2</sub>}Cl<sub>2</sub>(μ-Cl)]<sub>2</sub> and MAO**

A suspension of Cr{(ethyl)<sub>2</sub>PN(methyl)P(ethyl)<sub>2</sub>}Cl<sub>2</sub>(μ-Cl)]<sub>2</sub> (0.0075g, 0.020 mmol of Cr) in 10 ml of toluene was transferred to a 300 ml pressure reactor (autoclave)

containing toluene (100 ml) and MAO (6.0 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4000 kPa (40 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 3.06 g. The product distribution of this example is summarised in Table 1.

**Example 43. Preparation of the (ethyl)<sub>2</sub>PN(isopropyl)P(phenyl)<sub>2</sub> ligand**

N-(diphenylphosphino)methylamine (1.870g, 7.69 mmol) in toluene (15 ml) was slowly added to a solution of chlorodiethylphosphine (0.986, 7.92 mmol) in toluene (20 ml) and triethylamine (5 ml). The mixture was stirred overnight before being filtered through a glass fibre filter. The solvents were removed under vacuum and 10 ml of water was added. The product was extracted in petroleum ether (3 × 5 ml) and organics combined. Removal of the solvent under vacuum yielded 2.200g (86%) of the product. <sup>31</sup>P {H} NMR: 49, 43 ppm.

**Example 44: Ethylene tetramerisation reaction using Cr(2-ethylhexanoate)<sub>3</sub>, (phenyl)<sub>2</sub>PN(isopropyl)P(ethyl)<sub>2</sub> and MAO**

A solution of Cr(2-ethylhexanoate)<sub>3</sub> (0.002M in toluene, 10 ml, 0.020 mmol) and a solution of (phenyl)<sub>2</sub>PN(isopropyl)P(ethyl)<sub>2</sub> (0.004M in toluene, 5 ml, 0.020 mmol) were added to a 300 ml pressure reactor (autoclave) containing toluene (100 ml) and MAO (6.0 mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4000 kPa (40 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 10.83 g. The product distribution of this example is summarised in Table 1.

**Example 45: Ethylene tetramerisation reaction using Cr(2-ethylhexanoate)<sub>3</sub>, (phenyl)(ethyl)PN(methyl)P(ethyl)(phenyl) and MAO**

A solution of Cr(2-ethylhexanoate)<sub>3</sub> (0.002M in toluene, 15 ml, 0.030 mmol) and a solution of (phenyl)(ethyl)PN(methyl)P(ethyl)(phenyl) (0.00365M in toluene, 9 ml, 0.033 mmol) were added to a 300 ml pressure reactor (autoclave) containing toluene (100 ml) and MAO (9.0mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4000 kPa (40 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 0.897 g. The product distribution of this example is summarised in Table 1.

**Example 46: Ethylene tetramerisation reaction using  $\text{Cr}(\text{2-ethylhexanoate})_3$ ,  $(\text{phenyl})(\text{ethyl})\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of  $\text{Cr}(\text{2-ethylhexanoate})_3$  (0.002M in toluene, 15 ml, 0.030 mmol) and a solution of  $(\text{phenyl})(\text{ethyl})\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$  (0.034 mmol in 9 ml toluene) were added to a 300 ml pressure reactor (autoclave) containing toluene (100 ml) and MAO (9.0mmol) at 45°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4000 kPa (40 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 13.23 g. The product distribution of this example is summarised in Table 1.

**Example 47: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{P}(=\text{Se})\text{N}(\text{propyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 33.4 mg of  $(\text{phenyl})_2\text{P}(=\text{Se})\text{N}(\text{propyl})\text{P}(\text{phenyl})_2$  (0.066 mmol) in 15 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (75ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa (45 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 8.45 g. The product distribution of this example is summarised in Table 1.

**Example 48: Ethylene tetramerisation reaction using  $\text{Cr}(\text{acetylacetonate})_3$ ,  $(\text{phenyl})_2\text{PCH}_2\text{CH}_2\text{P}(\text{phenyl})_2$  and MAO**

A solution of 26.3 mg of  $(\text{phenyl})_2\text{PCH}_2\text{CH}_2\text{P}(\text{phenyl})_2$  (0.198 mmol) in 10 ml of toluene was added to a solution of 11.5 mg  $\text{Cr}(\text{acetylacetonate})_3$  (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4000 kPa (40 barg). The reaction was terminated after 30 min, and the procedure of Example 2 above was employed. The product mass was 21.23 g. The product distribution of this example is summarised in Table 1.